[Contribution from the Department of Chemistry,
Massachusetts Institute of Technology]

Displacement Reactions. XII.[1] Correlation of Rates of Solvolysis with a Four-Parameter Equation

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(1) Paper XI[2] serves as an introduction to this paper. This work was supported by the Office of Naval Research.

(2) C. G. Swain, R. B. Mosely, D. E. Bown, I. Allen and D. C. Dittmer, *J. Am. Chem. Soc.*, 76, 000 (1954).

By C. Gardner Swain, Robert B. Mosely
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A four-parameter equation, $\log (k/k^\circ) = c_1 d_1 + c_2 d_2$, is tested, where k is the first-order rate constant for solvolysis of any compound in any medium, k° is the corresponding rate constant in a standard medium (80% ethanol) at the same temperature, c_1 and c_2 are constants depending only on the compound undergoing solvolysis, and d_1 and d_2 are constants depending only on the medium. All available data capable of serving as a test of the equation were used. Values of c_1 and c_2 are reported for 25 compounds ranging from *p*-nitrobenzoyl chloride to triphenylmethyl fluoride, and values of d_1 and d_2 for 18 solvents ranging from methanol to formic acid. These were determined from the equation and 146 observed $\log (k/k^\circ)$ values by the method of least squares. The mean and maximum ranges in observed rate for a fixed compound are factors of 1.4×10^3 and 7.6×10^6 respectively. The mean and maximum errors in the calculated rate are factors of 1.33 and 4.4.

A four-parameter equation was developed in paper XI[2]

$$\log (k/k^\circ) = c_1 d_1 + c_2 d_2$$

where k is the first-order rate constant for solvolysis of any compound in any medium, k° is the corresponding rate constant in a standard medium at the same temperature, c_1 and c_2 are constants depending only on the compound undergoing solvolysis, and $\underline{d}_1$ and $\underline{d}_2$ are constants depending only on the solvent.

As the standard solvent we chose 80% ethanol-20% water by volume because more data were available for it than for any other solvent. Table I lists log $\underline{k}_o$ in 80% ethanol for 25 compounds.

Table II lists the 146 log ($\underline{k}/\underline{k}°$) values capable of serving as a check on the equation,[3] i.e., for solvents studied with three or more compounds

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(3) The only data knowingly omitted were 6 data on t-butyl bromide, which were used in preliminary attempts to fit the equation but were dropped in the course of the Mark IV calculation because they appeared to interfere with convergence of the successive approximation procedure employed.

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or for compounds studied in four or more solvents at the same temperature, or at enough temperatures to permit extrapolation to the common temperature for each compound listed in Table I.

Table I

RATES IN 80% ETHANOL

Compound[a]	$\log_{10}$ $\underline{k}°$, sec.$^{-1}$	Temp., °C.	Ref.
$NO_2\phi COCl$	-1.31	25	4
$NO_2\phi COF$	-2.00	25	4
$\phi COCl$	-2.59	25	4
ϕCOF	-4.21	25	4
$Me\phi COCl$	-2.46	25	4
$Me\phi COF$	-4.67	25	4
MeBr	-5.66	50	5,6
EtBr	-5.86	50	5,6
EtOTs	-5.04	50	5
n-BuBr	-5.41[b]	75.1	7
ϕCH_2Cl	-5.65	50	5
ϕCH_2OTs	-3.49	25	5
i-PrBr	-5.93	50	5
i-PrOBs	-2.77	70	8
PinOBs	-2.86	70	8
MeOCxOBs	-5.49	50	5
BrCxOBs	-5.15	50	5
$\phi CHClMe$	-3.79	50	9
ϕ_2CHCl	-2.77	25	10
ϕ_2CHF	-6.56	25	11
t-BuCl	-5.03	25	12
ϕ_3CSCN	-2.98[c]	25	11
ϕ_3COAc	-3.28	25	11
$\phi_3CO\phi NO_2$	-3.35	25	11
ϕ_3CF	-3.58	25	11

[a] ϕ = C_6H_5 or p-substituted C_6H_4; BrCx = trans-2-bromocyclohexyl; Pin = pinacolyl; OTs = p-toluenesulfonate; OBs = p-bromobenzenesulfonate; Me, Et, Pr, Bu = CH_3, C_2H_5, C_3H_7, C_4H_9.

[b] Interpolated from a plot of log k vs. mole fraction of water.

[c] Assumed value. No measurements were made in 80% ethanol.

(4) D. E. Bown, Ph.D. Thesis, M.I.T., April, 1953.

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(6) L. C. Bateman, K. Cooper, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 925 (1940).

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(8) E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70, 846 (1948).

(9) A. M. Ward, J. Chem. Soc., 445 (1927).

(10) A. M. Ward, ibid., 2285 (1927).

(11) C. G. Swain and R. B. Mosely, J. Am. Chem. Soc., 76, 0000 (1954); R. B. Mosely, Ph.D. Thesis, M.I.T., July, 1952.

(12) E. D. Hughes, J. Chem. Soc., 255 (1935).

Table II

RELATIVE RATES OF SOLVOLYSIS[a]

Compound[b]	Solvent[c]	log (k/k°)[a]	Ref.
$NO_2\phi COCl$	EtOH, 100	-0.68	4
"	Me_2CO, 90	- .91	4
"	Me_2CO, 80	- .52	4
"	Me_2CO, 70	- .35	4
"	Me_2CO, 50	- .12	4
"	AcOH, 100	-4.67	4
"	HCOOH, 100	-3.37	4
$NO_2\phi COF$	MeOH, 100	-1.59	4
"	MeOH, 96.7	-0.51	4
"	MeOH, 69.5	+ .47	4
"	EtOH, 100	-1.77	4
"	EtOH, 40	+0.51	4
"	Me_2CO, 80	-1.07	4
"	Me_2CO, 70	-0.64	4
"	Me_2CO, 50	-0.04	4
"	AcOH, 100[d]	-6.37	4
"	HCOOH, 100	-4.25	4
$\phi COCl$	MeOH, 100	+0.22	13
"	MeOH, 96.7	+ .33	4
"	MeOH, 69.5	+ .87	4
"	EtOH, 100	- .52	4
"	EtOH, 60	+ .48	4
"	EtOH, 50	+ .84	4
"	EtOH, 40	+1.30	4
"	Me_2CO, 90	-1.18	4
"	Me_2CO, 80	-0.72	4

(Table II continued)

Compound	Solvent	log ($\underline{k}/\underline{k}^{\circ}$)	Ref.
ϕCOCl	Me_2CO, 70	-0.37	4
"	Me_2CO, 50	+ .50	4
"	AcOH, 100	-2.39	4
ϕCOF	MeOH, 96.7	-0.23	4
"	MeOH, 69.5	+ .84	4
"	EtOH, 100	-1.58	4
"	EtOH, 40	+0.81	4
"	Me_2CO, 80	-1.19	4
"	Me_2CO, 70	-0.67	4
"	Me_2CO, 50	+ .11	4
"	AcOH, 100[d]	-4.47	4
"	HCOOH, 100	-1.61	4
MeϕCOCl	EtOH, 100	-0.79	13
"	Me_2CO, 80	- .90	4
"	Me_2CO, 50	+ .85	4
"	AcOH, 100	-1.94	4
MeϕCOF	Me_2CO, 80	-1.13	4
"	Me_2CO, 50	+0.09	4
"	AcOH, 100[d]	-3.79	4
"	HCOOH, 100	-0.36	4
MeBr	EtOH, 100	- .75	5
"	EtOH, 50	+ .41	5,14
"	Me_2CO, 50	+ .22	29
"	H_2O, 100	+ .68	5
"	HCOOH, 100[e]	-1.78	5,16

(Table II continued)

Compound	Solvent	log (k/k°)	Ref.
EtBr	EtOH, 100	-0.77	5,17
"	EtOH, 50	+ .58	5,14
"	H_2O, 100	+1.12	5
"	HCOOH, 100[f]	-1.15	5,17
EtOTs	MeOH, 100	-0.28	5
"	EtOH, 100	- .57	5
"	EtOH, 50	+ .37	5
"	AcOH, 100	-2.38	5
n-BuBr	MeOH, 100[g]	-0.36	7
"	MeOH, 96.7[g,h]	- .21	7
"	MeOH, 69.5[g,h]	+ .46	7
"	EtOH, 100	- .70	7
"	EtOH, 90[h]	- .19	7
"	EtOH, 60[h]	+ .27	7
"	HCOOH, 100[g]	-1.14	18
ϕCH_2Cl	MeOH, 100	-0.26	5
"	EtOH, 100	- .85	5
"	EtOH, 50	+ .74	5
ϕCH_2OTs	MeOH, 100	- .29	5
"	EtOH, 100	- .78	5
"	AcOH, 100	-2.09	5
i-PrBr	EtOH, 100	-1.02	5
"	EtOH, 50	+0.86	5
"	H_2O, 100	+1.99	5
"	HCOOH, 100	-0.14	5
i-PrOBs	MeOH, 100	- .37	8
"	EtOH, 100	- .81	8
"	AcOH, 100	-1.39	8
"	Ac_2O, 97.5	-3.08	8

(Table II continued)

Compound	Solvent	log (k/k°)	Ref.
PinOBs	MeOH, 100	-0.63	8
"	EtOH, 100	-1.29	8
"	AcOH. 100	-0.70	8
"	Ac_2O, 97.5	-2.08	8
"	HCOOH[i]	+2.39	8
MeOCxOBs	MeOH, 100	-0.46	5
"	EtOH, 100	-1.02	5
"	EtOH, 50	+0.70	5
"	AcOH, 100	- .97	5,19
BrCxOBs	MeOH, 100	- .74	5
"	EtOH, 100	-1.42	5
"	EtOH, 50	+1.11	5
"	AcOH, 100	-1.12	5,19
ØCHClMe	MeOH, 100[j,k]	-0.43	20
"	EtOH, 100[j,m]	-1.50	20
"	Me_2CO, 80[j,n]	-1.12	20
"	AcOH, 100	-1.62	21
$Ø_2CHCl$	MeOH, 96.7	-0.07	11
"	EtOH, 100	-1.51	22
"	EtOH, 90	-0.55	10
"	Me_2CO, 90	-2.57	23
"	Me_2CO, 80	-1.38	23
"	Me_2CO, 70	-0.73	23
"	Me_2CO, 50	+0.98	15
"	AcOH, 100[p]	-2.36	11
"	HCOOH, 83.3	+2.61	11

(Table II continued)

Compound	Solvent	log (*k*/*k*°)	Ref.
ϕ_2CHF	EtOH, 50	+1.61	11
"	AcOH, 100[p]	+2.11	11
"	HCOOH, 83.3	+5.90	11
t-BuCl	MeOH, 100	-1.05	24
"	MeOH, 96.7	-0.72	24
"	MeOH, 69.5	+1.02	24
"	EtOH, 100	-1.98	12
"	EtOH, 90	-0.73	12
"	EtOH, 60	+1.14	12
"	EtOH, 50	+1.60	12
"	EtOH, 40	+2.15	12
"	Me_2CO, 80	-0.68	12
"	Me_2CO, 50	+1.29	25
"	H_2O, 100	+3.55	8,26
"	AcOH, 100	-1.64	8
"	Ac_2O, 97.5	-3.29	8
"	HCOOH, 83.3	+1.50	11
"	HCOOH, 100	+2.08	18
ϕ_3CSCN	MeOH, 96.7	- .30	11
"	MeOH, 69.5	+ .40	11
"	EtOH, 40	+ .56	11
"	Me_2CO, 80	- .28	11
"	Me_2CO, 70	- .05	11
"	Me_2CO, 50	+ .26	11

(Table II continued)

Compound	Solvent	log ($k/k°$)	Ref.
ϕ_3COAc	MeOH, 96.7	+0.03	11
"	MeOH, 69.5	+ .90	11
"	EtOH, 60	+ .56	11
"	Me_2CO, 80	-1.56	11
"	Me_2CO, 50	+0.14	11
$\phi_3CO\phi NO_2$	MeOH, 69.5	+ .83	11
"	EtOH, 40	+1.25	11
"	Me_2CO, 50	+0.37	11
"	AcOH, 100^P	+ .97	11
ϕ_3CF	MeOH, 96.7	+ .11	11
"	MeOH, 69.5	+1.50	11
"	EtOH, 100	-1.73	11
"	EtOH, 40	+2.02	11
"	Me_2CO, 70	-1.21	11
"	Me_2CO, 50	+0.58	11
"	AcOH, 100^P	+1.76	11

(Footnote to Table II)

[a]These are decimal logarithms. For all compounds, log $\underline{k}/\underline{k}°$ = 0.000 in 80% ethanol by definition. For each compound, the temperature is that given in Table I.

[b]Symbols for compounds are explained in footnote a of Table I.

[c]Number after solvent is % by volume based on volumes before mixing; the residue is water except for 97.5% Ac_2O which is 2.5% AcOH; Me, Et, Ac = CH_3, C_2H_5, CH_3CO.

[d]Calculated from data at 80° and 100°.

[e]Extrapolated from a higher temperature using ΔE = 20.2 kcal.[27]

[f]Extrapolated from a higher temperature using ΔE = 19.8 kcal.[27]

[g]Extrapolated from a higher temperature using ΔE = 22.0 kcal.[11]

[h]Interpolated from a plot of log $\underline{k}$ vs. mole fraction of water.

[i]Extrapolated from a lower temperature using ΔE = 27.1 kcal.[28]

[j]Unfortunately the values used in these calculations were not the correct ones recorded here but were -1.37, -2.45 and -2.06 for methanol, ethanol, and 80% acetone respectively, which correspond to incorrectly calculated values tabulated by others[8] in the literature. We discovered this error subsequent to completion of the calculation.

[k]Extrapolated from a higher temperature using E = 21.7 kcal.[27]

[m]Extrapolated from a higher temperature using E = 21.9 kcal.[27]

[n]Extrapolated from a higher temperature using E = 21.8 kcal.[27]

[p]The datum given was obtained in 99.3% AcOH - 0.7% Ac_2O, but is used for 100% AcOH since this compound is relatively little affected by traces of H_2O or Ac_2O.

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(14) I. Dostrovsky and E. D. Hughes, J. Chem. Soc., 164 (1946).

(15) C. G. Swain, C. B. Scott and K. Lohmann, J. Am. Chem. Soc., 75, 136 (1953).

(16) I. Dostrovsky and E. D. Hughes, J. Chem. Soc., 166, 171 (1946).

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(18) L. C. Bateman and E. D. Hughes, J. Chem. Soc., 935, 940, 945 (1940).

(19) S. Winstein, E. Grunwald and L. Ingraham, J. Am. Chem. Soc., 70, 821 (1948).

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(22) E. D. Hughes, C. K. Ingold and N. A. Taher, J. Chem. Soc., 949 (1940).

(23) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, ibid., 979 (1940).

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(26) C. G. Swain and S. D. Ross, J. Am. Chem. Soc., 68, 658 (1946).

(27) E. D. Hughes, C. K. Ingold, S. Masterman and B. J. McNulty, J. Chem. Soc., 899 (1940).

(28) S. Winstein and H. Marshall, J. Am. Chem. Soc., 74, 1120 (1952).

(29) C. G. Swain and C. B. Scott, ibid., 75, 141 (1953).

The data represent a wide range of structural variation. The compounds range from p-nitrobenzoyl and methyl to triphenylmethyl and from fluorides to arylsulfonates. Some have strong neighboring group participation and the pinacolyl compound even rearranges. The solvents range from anhydrous alcohols and water to glacial acetic acid and anhydrous formic acid.

Wishing to weight all the log ($\underline{k}/\underline{k}°$) values equally, we chose the condition

$$\sum_{146\ \text{data}} [\log (\underline{k}/\underline{k}°)_{\text{obs.}} - (\underline{c}_1\underline{d}_1 + \underline{c}_2\underline{d}_2)] = \text{minimum}$$

to define the best fit. Thus no compound is given more weight than any other. Setting the partial derivative with respect to each other of the 25 $\underline{c}_1$, 25 $\underline{c}_2$, 17 $\underline{d}_1$ and 17 $\underline{d}_2$ unknown parameters equal to zero gave 84 simultaneous equations. These were solved by an interative procedure (see method of calculation below) on the Mark IV digital computer of the Harvard Computation Laboratory.

The solution obtained was not unique. To make it unique it was necessary subsequently to impose four conditions (in addition to $\underline{d}_1 = \underline{d}_2 = 0.00$ for 80% ethanol). These are in the nature of scale factors or normalization conditions for the calculated parameters and were chosen arbitrarily as follows.

$$\underline{c}_1 = 3.00\ \underline{c}_2 \text{ for MeBr}$$

$$\underline{c}_1 = \underline{c}_2 = 1.00 \text{ for } \underline{t}\text{-BuCl}$$

$$3.00\ \underline{c}_1 = \underline{c}_2 \text{ for } \phi_3\text{CF}.$$

A renormalization to any other arbitrary assignment (any $\underline{\alpha}$ or $\underline{\beta}$) may be made easily using the equations

$$c_1^* = \alpha c_1 + (1 - \alpha) c_2$$

$$c_2^* = \beta c_1 + (1 - \beta) c_2$$

$$d_1^* = \left(\frac{1 - \beta}{\alpha - \beta}\right) d_1 + \left(\frac{- \beta}{\alpha - \beta}\right) d_2$$

$$d_2^* = \left(\frac{\alpha - 1}{\alpha - \beta}\right) d_1 + \left(\frac{\alpha}{\alpha - \beta}\right) d_2$$

$$d_1^* + d_2^* = d_1 + d_2$$

for new values (denoted by superscript stars).

Table III lists the values of the constants obtained. The values in parentheses are the ones arbitrarily assigned. Values based on very limited data are indicated by superscript letters referring to explanatory notes.

The ratio c_1/c_2 is a convenient single number to characterize the reactivity of a compound. Compounds which discriminate relatively more highly among electrophilic reagents than among nucleophilic reagents tend to have low values for this ratio. As expected, this ratio decreases from p-nitro to p-methyl and in the order methyl, ethyl, i-propyl, t-butyl, benzhydryl, trityl.

The difference $d_1 - d_2$ is a convenient single number to characterize the reactivity of a solvent. The most electrophilic solvents have the lowest values for this difference, with the difference decreasing in the order anhydrous alcohols, acetone-water and alcohol-water mixtures, water, glacial acetic acid, anhydrous formic acid.

Fig. 1 shows the correlation for several typical compounds using these compound and solvent constants.

Table III

VALUES OF COMPOUND AND SOLVENT CONSTANTS

Compound	c_1	c_2	c_1/c_2	Compound	c_1	c_2	c_1/c_2
$NO_2\phi COCl$	1.09	0.21	5.2	i-PrOBs	0.63	0.48	1.33
$NO_2\phi COF$	1.67	.49	3.4	MeOCxOBs	.57	.57	1.00
$\phi COCl$	0.81	.52	1.6	BrCxOBs	.80	.87	0.92
ϕCOF	1.36	.66	2.1	PinOBs	.76	.87	0.86
$Me\phi COCl$	0.82	.65	1.3	$\phi CHClMe$	1.47	1.75	.84
$Me\phi COF$	1.29	.80	1.6	ϕ_2CHCl	1.24	1.25	.99
MeBr	0.80	.27	(3.0)	ϕ_2CHF	0.32[a]	1.17[a]	.27[a]
EtBr	.80	.36	2.2	t-BuCl	(1.00)	(1.00)	(1.00)
EtOTs	.65	.24	2.7	ϕ_3CSCN	0.19	0.28	0.69
n-BuBr	.77	.34	2.2	ϕ_3COAc	2.19[b]	.77[b]	—
ϕCH_2Cl	.74[a]	.44[a]	1.7[a]	$\phi_3CO\phi NO_2$	0.18	.59	.31
ϕCH_2OTs	.69[a]	.39[a]	1.8[a]	ϕ_3CF	.37	1.12	(.33)
i-PrBr	.90	.58	1.5				

Solvent	d_1	d_2	d_1-d_2	Solvent	d_1	d_2	d_1-d_2
MeOH, 100	-0.05	-0.73	+0.68	Me_2CO, 90	-0.53[c]	-1.52[c]	+ 1.0[c]
MeOH, 96.7	- .11	- .05	- .06	Me_2CO, 80	- .45	-0.68	+ 0.2
MeOH, 69.5	- .06	+1.32	-1.38	Me_2CO, 70	- .09[c]	- .75[c]	+ .7[c]
EtOH, 100	- .53	-1.03	+0.49	Me_2CO, 50	- .25	+ .97	- 1.2
EtOH, 90	- .01[c]	- .54[c]	+ .52[c]	H_2O, 100	-.44[d]	+4.01[d]	- 4.5[d]
EtOH, 80	(.00)	(.00)	(.00)	AcOH, 100	-4.82	+3.12	- 7.9
EtOH, 60	- .22[d]	+1.34[d]	-1.56[d]	Ac_2O, 97.5	-8.77[c]	+5.34[c]	-14.1[c]
EtOH, 50	+ .12	+1.33	-1.21	HCOOH, 83.3	-4.44[c]	+6.26[c]	-10.7[c]
EtOH, 40	- .26	+2.13	-2.38	HCOOH, 100	-4.40	+6.53	-10.9

(Footnotes to Table III)

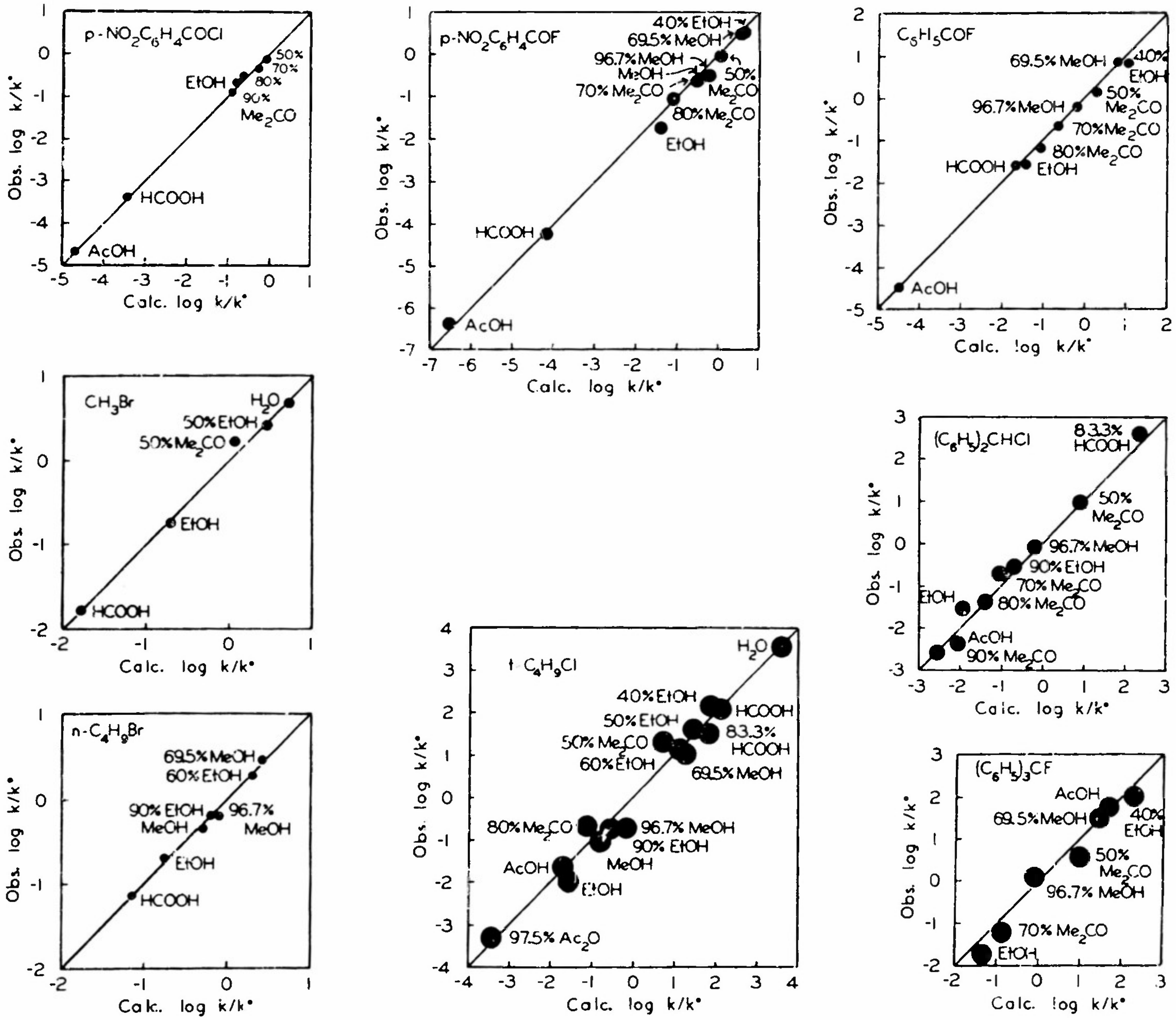
[a]Somewhat doubtful because based on only three log ($\underline{k}/\underline{k}°$) values.

[b]Especially badly fixed by the data because based on only five log ($\underline{k}/\underline{k}°$) values for very similar media: none was an absolute alcohol or contained over 50% water or any acetic acid or formic acid.

[c]Use with caution. Not well fixed by the data because based on only three compounds.

[d]Based on only four compounds.

[e]Based on aromatic compounds only, hence may give poor predictions for aliphatic compounds.



p-NO2C6H4COCl
50%
70%
80%
90%
Me2CO
EtOH
HCOOH
AcOH
Obs. log k/k°
Calc. log k/k°
p-NO2C6H4COF
40% EtOH
69.5% MeOH
96.7% MeOH
MeOH
70% Me2CO
50% Me2CO
80% Me2CO
EtOH
HCOOH
AcOH
Obs. log k/k°
Calc. log k/k°
C6H5COF
69.5% MeOH
40% EtOH
50% Me2CO
96.7% MeOH
70% Me2CO
80% Me2CO
HCOOH
EtOH
AcOH
Obs. log k/k°
Calc. log k/k°
CH3Br
H2O
50% EtOH
50% Me2CO
EtOH
HCOOH
Obs. log k/k°
Calc. log k/k°
(C6H5)2CHCl
83.3% HCOOH
50% Me2CO
96.7% MeOH
90% EtOH
70% Me2CO
EtOH
80% Me2CO
AcOH
90% Me2CO
Obs. log k/k°
Calc. log k/k°
n-C4H9Br
69.5% MeOH
60% EtOH
90% EtOH
MeOH
96.7% MeOH
EtOH
HCOOH
Obs. log k/k°
Calc. log k/k°
t-C4H9Cl
H2O
40% EtOH
HCOOH
50% EtOH
83.3% HCOOH
50% Me2CO
60% EtOH
69.5% MeOH
80% Me2CO
96.7% MeOH
90% EtOH
MeOH
AcOH
EtOH
97.5% Ac2O
Obs. log k/k°
Calc. log k/k°
(C6H5)3CF
AcOH
69.5% MeOH
40% EtOH
50% Me2CO
96.7% MeOH
70% Me2CO
EtOH
Obs. log k/k°
Calc. log k/k°

Table IV lists some measures of fit.[2] The compound with the largest ϵ (mean error in log $k_{calc.}$) is t-butyl chloride and for it our measure of fit,[2] Φ, is typical and excellent, viz. 85%. Figs. 1 - 8 show typical plots of the fits obtained. The largest individual error is for benzoyl chloride in methanol and corresponds to a factor of 4.4 in k. The mean ϵ for all compounds is 0.124 (factor of 1.33 error in k). For typical solvents ϵ is 0.12 for methanol (n = 12), 0.22 for 50% acetone (n = 13), 0.07 for acetic acid (n = 18), and 0.04 for formic acid (n = 10). The fit is about as good for the extreme compounds and solvents studied as for the ones of intermediate reactivity.

Table IV

MEASURES OF FIT[2] FOR CERTAIN COMPOUNDS

Compound	n	ϵ	Φ, %
$NO_2\phi COCl$	7	0.07	95
$NO_2\phi COF$	10	.15	90
$\phi COCl$	12	.23	72
ϕCOF	9	.11	91
MeBr	5	.06	93
n-BuBr	7	.05	89
$\phi CHCl$	9	.19	84
t-BuCl	15	.25	85
ϕ_3CF	7	.25	79

Discussion.- The results were compared with those using other equations in paper XI.[2] The correlation is particularly gratifying for p-nitrobenzoyl chloride and triphenylmethyl fluoride, which gave almost random scatter plots[11] of log $(\underline{k}/\underline{k}^\circ)_{obs.}$ vs. log $(\underline{k}/\underline{k}^\circ)_{calc.}$ when using the equation log $(\underline{k}/\underline{k}^\circ) = \underline{m}\underline{Y}$.

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METHOD OF CALCULATION

In this problem it is required to find the best values of $\underline{a}_i$, $\underline{b}_i$, $\underline{c}_j$, $\underline{d}_j$ to represent a given matrix of the form $E_{ij}Z_{ij}$ by the scalar product

$$Z_{ij} \doteq \underline{a}_i\underline{c}_j + \underline{b}_i\underline{d}_j, \qquad i = 1,2,\ldots,\underline{m}$$
$$j = 1,2,\ldots,\underline{n}.$$

Not all possible elements Z_{ij} are given; the elements E_{ij} are introduced to form an existence matrix such that $E_{ij} = 1$ if the corresponding Z_{ij} is given and $E_{ij} = 0$ otherwise.

To obtain a least squares fit, it is required that the quantity

$$\epsilon^2 = \sum_i \sum_j E_{ij}(Z_{ij}-\underline{a}_i\underline{c}_j-\underline{b}_i\underline{d}_j)^2$$

be minimum. From this it follows that

$$\frac{\partial}{\partial \underline{a}_i}(\epsilon^2) = \frac{\partial}{\partial \underline{b}_i}(\epsilon^2) = \frac{\partial}{\partial \underline{c}_j}(\epsilon^2) = \frac{\partial}{\partial \underline{d}_j}(\epsilon^2) = 0$$

for all i and j. Carrying out the differentiations one obtains a system of 2 $(\underline{m}+\underline{n})$ non-linear simultaneous equations as follows:

$$a_i \sum_j E_{ij} c_j^2 + b_i \sum_j E_{ij} c_j d_j = \sum_j E_{ij} c_j Z_{ij} \tag{1}$$

$$a_i \sum_j E_{ij} c_j d_j + b_i \sum_j E_{ij} d_j^2 = \sum_j E_{ij} d_j Z_{ij} \tag{2}$$

$$c_j \sum_i E_{ij} a_i^2 + d_j \sum_i E_{ij} a_i b_i = \sum_i E_{ij} a_i Z_{ij} \tag{3}$$

$$c_j \sum_i E_{ij} a_i b_i + d_j \sum_i E_{ij} b_i^2 = \sum_i E_{ij} b_i Z_{ij}. \tag{4}$$

If approximations to the values of c_j and d_j be given, Equations (1) and (2) can be solved simultaneously to give approximate values of a_i and b_i. Then Equations (3) and (4) can be solved to give new approximations to the values of c_j and d_j. This is a simple process since, for a given value of i, Equations (1) and (2) are just a pair of linear simultaneous equations involving a_i and b_i as unknowns, and a similar remark applies to Equations (3) and (4).

Although Equations (1), (2), (3) and (4) may be used as an iterative process to obtain a solution of the problem it was decided to employ an extrapolation process[30] in order to decrease the time required

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(30) The principle on which this process is based was suggested by Dr. R. E. Clapp.

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to obtain the answer. Let the sets of numbers a_i, b_i, c_j and d_j obtained after the n-th iteration form the vector V_n. Let

$$V_{n+1} - V_n = D_n.$$

Now ϵ^2 may be written as

$$\epsilon^2 = f(V_{n+1})$$

since ϵ^2 is a function of the variables which form the components of V_n.

One may calculate

$$f_0 = f(V_{n+1})$$

$$f_1 = f(V_{n+1} + hD_n)$$

$$f_2 = f(V_{n+1} + 2hD_n)$$

where h is a scalar. Now assume that $f(V_{n+1} + xD_n)$ is approximately a quadratic in x (in practice the validity of this assumption depends mainly on the choice of h).

Then

$$f(V_{n+1} + xD_n) \doteq f_0 + u\Delta f + \frac{u(u-1)}{2} \Delta^2 f$$

where

$$u = \frac{x}{h}, \quad \Delta f = f_1 - f_0, \quad \Delta^2 f = f_2 - 2f_1 + f_0.$$

This expression of f may now be minimized with respect to x by setting the derivative equal to zero.

One finds that $f(V_{n+1} + sD_n)$ is mininum for

$$s = h\left(\frac{1}{2} - \frac{\Delta f}{\Delta^2 f}\right),$$

and the vector $V = V_{n+1} + sD_n$ may be used to start a new series of iterations. In the course of the problem values of s of 10-20 were usual, although much larger numbers were encountered in certain circumstances. The size of s is, of course, dependent to some extent on the number of iterations between extrapolations. This number was varied somewhat in the course of running the problem, though it was usually found that three to five iterations gave good results. Running time for this problem, starting either with given approximations or with all starting values equal to unity, was about one hour.

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